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Critical Oxygen (Flammability) Index of Hydraulic Fluids - Preliminary Trials

By

N. K. Sarin *

Abstract

This investigation is the first attempt at MRL to apply the critical oxygen index of flammability method to hydraulic fluids in order to determine their relative fire-resistance in quantitative terms and to provide a more efficient means of detecting qualitative changes in the product formulations.

An ASTM standard (D2863) test procedure was modified slightly, using an asbestos tape soaked in hydraulic oil and held vertically in a glass tube reservoir before igniting it inside a controlled atmosphere of oxygen and nitrogen. Preliminary trials indicate that this procedure can be employed to determine relative oxygen index of flammability for almost all types of hydraulic fluids. Although the oxygen indices may not represent absolute values due to a change in the standard procedure, a relative measure of the fire-resistance can be achieved.

Further studies are recommended to refine the proposed procedure.

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* Investigation Officer, Energy, Mines and Resources Canada, Canada Centre for Mineral and Energy Technology, Mining Research Laboratories, Canadian Explosive Atmospheres Laboratory, Ottawa, Ontario.

Keywords: hydraulic fluids, fire-resistance, flammability, oxygen index, testing, procedure, standards, quality assurance, mine, safety. and Resources Dept.

CRITICAL OXYGEN (FLAMMABILITY) INDEX OF HYDRAULIC FLUIDS - PRELIMINARY TRIALS

N.K. SARIN

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Introduction

The critical oxygen index (O/I) of flammability is one measure of the relative fire-resistance characteristic of materials by measuring the minimum concentration of oxygen required in a mixture of oxygen (O_2) and nitrogen (N) that will just barely support combustion. In short, it is expressed as $O/I = O_2/(O_2 + N)$. This oxygen concentration in a vertically rising mixture of oxygen and nitrogen, is measured under equilibrium of a candle-like burning i.e. the energy generated from the combustion process should be equal to the energy lost to the surroundings, which establishes a thermal equilibrium (1).

Since the O/I value is based upon an energy balance, any process which radically alters that balance will alter the results; however, the power of the O/I is that only a radical change in the energy balance will lead to a major change in the test results. Developed in the mid 1960's, the oxygen index test has proved to be a convenient quantitative measure which is reproducible of polymer flammability.

Until recently, the oxygen index method was employed mainly for self-supporting materials. Investigators and researchers at General Electric Co in the U.S. have applied this technique to many liquids and achieved considerable success. Subsequent to this work, some other investigators have used this technique employing a glass wick to study oxygen indices of selected organophosphorous materials. The General Electric workers simply replaced the usual polymer candle with a small 2 cm^3 ceramic reservoir in which the liquid or a fusible solid is placed for testing. The flame was fed directly from the surface of the liquid reservoir, a condition which closely approximates a real life fire situation involving liquid materials.

The concept of flammability limit is used to describe conditions for which combustion will or will not take place. In some cases, determination of O/I depends on oxidizer flow, test configurations and fuel geometry as well as ambient temperature and pressure. The oxygen index unlike many other go/no-go type flammability tests can be used to gain a better insight into the overall combustion process.

The most important aspect of the oxygen index method, unlike the other small scale tests, is that O/I is not a direct measure of volatility and/ or ease of ignition, but rather a measure of flame propagation and extinction phenomenon (1). Due to the convenience and reliability of this test, it can serve well for quality assurance checks and as a research tool for the development of fire-resistant products.

Background

In a mining environment, varieties of hydraulic fluids are employed extensively for hydraulically powered machines. Fires and explosions are the major concern resulting from the use of such fluids, particularly in the underground mines. The Canadian Explosive Atmospheres Laboratory (CEAL) evaluates these products in accordance with CSA standard M423-87 and monitors the consistency of the approved products periodically through a quality assurance program. In order to minimize the cost of re-evaluations of such products, and to obtain more reproducible test results, this investigation is the first attempt at CEAL to determine suitability of the oxygen index method for this purpose.

Until recently at CEAL, the flammability of mine hydraulic fluids has been determined by a spray ignition test and a wick test similar to the practice at the National Coal Board (NCB). The spray test involves recording of the duration of combustion of the atomized spray after the ignition source has been removed. In the case of the wick test, an asbestos tape 25 mm wide x .40 mm thick is stretched horizontally in a bath of fluid under test and the exposed edge of the wick is ignited with a small propane torch using different flame exposure times under normal atmospheric conditions. However, in the case of wick and spray tests, some variations in the test results have been noticed using the same product at different times. This indicates relatively low reliability compared to the oxygen index tests.

The author has already applied the oxygen index method to polymeric plastic materials used for construction of mine ventilation materials and conveyor belt products. This experience has been extremely useful, particularly for quality control checks and verification of material composition,

once the product has been approved and certified after the series of flammability tests mentioned above.

Attempts were made to obtain the apparatus used by General Electric for the study of oxygen indices, without any success. Therefore, at CEAL we decided to use asbestos tapes 25 mm x .40 mm thick x 175 mm long held vertically in a vaccutainer glass tube (12 mm dia x 300 mm) filled with the test fluid at room temperature. Part of the tape was projecting above the top opening of the tube, for ease of ignition. We have tested about thirteen fluids covering four main categories and found that aqueous based fluids took much longer to ignite, whereas it is relatively quicker to ignite and determine O/I numbers for synthetic oils, including phosphate esters and blends of hydrocarbons.

It is hoped that further work on this subject will assist in replacing the existing mandatory wick flammability test for certification, with a more reliable test such as the oxygen index test.

Apparatus

An oxygen index tester model number 8100, produced by United States Testing Co Inc, New Jersey, was employed after making necessary changes to the specimen holder (Refer to figures 1 & 2). This apparatus is normally used to determine oxygen indices of plastic materials in accordance with the ASTM standard D2863.

General Description

The specimen is held in a vertical position inside a glass test column. Gases enter the test

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National Coal Board, UK. (Now renamed as British Coal)

CEAL- Canadian Explosive Atmospheres Laboratory.

CSA- Canadaian Standards Association.

ASTM- American Society for Testing and Materials.

column through the metal base which contains a bed of glass beads to mix and distribute the oxygen and nitrogen. When the flow of rising gas mixture has stablized in the column, the specimen is ignited and observed for flame propagation and the duration of burning. The test is repeated with a fresh sample under different oxygen concentrations until the combustion is barely sustained for three minutes or it propagates about 75 mm in length. This concentration of oxygen establishes the required index.

Test Column

The column is a portable enclosure made of a heat resistant glass, 75 mm inside diameter and 45 $\pm$ 2 cm in height. The lower part of the column is metallic base which contains glass beads (3 to 5 mm in diameter and stacked about 10 cm deep). The beads assist mixing and even distribution of the gases around the test specimen. A wire screen is placed above the glass beads to trap any falling fragments from the burning material.

Specimen Holder

A 12 mm diameter x 300 mm long vaccutainer tube is held vertically in a steel cup coated with silicon for a snug fit. The tube is filled with the hydraulic fluid sample and an asbestos tape, 25 mm wide x .40 mm thick x 125 mm in length is held vertically inside the tube projecting about 5 cm outside the tube. The tape is kept in semicircular shape to give it some stiffness and to make it more self-supporting.

Gas Supply

Commercial grade (99 %) or better is used for the oxygen and nitrogen. No air supply is mixed with the gases. The supply pressure in both cases is maintained around 3.394 Bars (50 psi).

Flowmeters

The flowmeters supplied with the apparatus are each equipped with an inline filter, dual floats and a dual direct reading scale in cm^3/s. Both floats are calibrated to $\pm$ 1% of full scale. Each flowmeter is also equipped with an integral flow controller and a needle valve which maintains a constant rate of flow independent of the upstream pressure changes. A toggle shut off valve is also provided on each unit to allow adjustment of one flowmeter at a time.

Ignition Source

The igniter is a 6-12 mm long flame of methane gas passing through a 1.6 mm diameter steel tube. The flow is controlled by a needle valve and the pressure is kept below 0.68 Bar (10 psi).

Soot, Fume and Heat Removal

To ensure removal of toxic fumes, soot and heat and other possible noxious products, the apparatus is installed under a fume hood, providing adequate ventilation.

The Specimens

Approximately 8 cm^3 of test fluid is poured into the vaccutainer tube at room temperature and a standard asbestos tape, with its combustibles removed (similar to NCB wick test), is held vertically projecting partly above the tube opening so long as the tape is self supporting. Refer to Figure 4.

Test Procedure

Basically the ASTM standard D2863 test procedure was followed with the following changes.

The asbestos tape was left soaking in a test fluid for at least 60 minutes. It was then transferred

to the vaccutainer tube containing 8 cm^3 of the test fluid at room temperature ($\sim 22°C$), after loading the tube in the holder. The tape was pulled out, about 5 cm projecting above the tube before ignition of the sample at the top. The duration of combustion was recorded after the ignition torch was removed in each trial. The length of flame propagation was also recorded in each trial for every fluid sample.

Initially the ignition was attempted in ambient air. If no ignition occured, the oxygen concentration was increased in gradual steps until the combustion was barely sustained for three minutes; otherwise the concentration was decreased in the same manner. The flow meters for O_2 and N were set according to the desired concentration (see table 3). The sum of the volumetric flows from both gases was maintained to correspond with a gas velocity of 4 cm/s in the test column.

The test procedure had to be varied slightly in the case of water-in-oil emulsion fluids, since ignition was not achieved with ease. After initial setting of the flow of both gases to a desired concentration,the nitrogen supply was cut off. Once the ignition took place in a purely oxygen atmosphere, the nitrogen content was gradually increased to reach the initial setting. Whenever the flame reached the top of the vaccutainer tube, the tape was pulled out to allow for 3 minutes of burning and to prevent cracking of the tube. This was more or less a "hit and miss" process.

A new asbestos tape was used for each trial, however the sample of the fluid remained the same until an O/I was established. Generally it took an average of 6-8 trials before the exact O/I became apparent. The criteria was that if the flame lasted more than 3 minutes, another trial was necessary under a different oxygen concentration. The tests were terminated whenever the combustion would be barely maintained for three minutes, indicating that the O/I number was established.

Observations, Analysis and Discussion

A total of 12 hydraulic fluids, which had already been evaluated under the certification program,

were investigated. Four of these were non-aqueous, mostly in the phosphate ester category; four belonged to the glycol series and the remaining were water-in-oil emulsions.
The flame exposure time to start ignition for the ester fluids was minimal at 2-5 seconds and an average of 7 trials was necessary to reach a conclusion for each fluid sample. One of the organic esters, fluid #31, burned violently until the oxygen concentration was reduced to 18.5% by volume. This result agrees with an earlier study using the standard wick test as per the CSA standard M423, resulting in its rejection for mine use. Obviously, any product which requires an oxygen concentration for combustion, less than that present in the normal atmosphere (21%), would be undesirable. The lower the O/I number, the less it would become acceptable from the safety point of view. In fact, for an added factor of safety, the cut off point should be much higher than 21% if the procedure is to be used for certification and approval.

The glycol category of fluids needed 8-10 seconds of flame exposure time before ignition could start. Only an average of 5 trials was necessary to determine the O/I number. In general the indices for these fluids were much higher than those observed for synthetic oils and emulsion fluids. These indices ranged between 28-30; indicating a good degree of fire-resistance. Similar results were obtained from earlier investigations using the standard wick test.

The flame contact times for emulsion type fluids varied between 10 to 20 s. The obvious reason for this excessive energy input before ignition is that part of the energy is consumed by the water content in evaporation before the combustible portion ignited. This phenomenon was almost absent with water glycols since water and glycols are miscible fluids. Moreover, the water-in-oil emulsions tend to rise quickly to the upper level due to capilliary action and needs to be evaporated by external energy before the combustible oil can catch fire. The average number of test trials was 5 and the oxygen indices ranged between 22.5 and 24.3.

Comparison of the O/I indices with the results of the standard wick test (Table 1) shows that most of the fluids with O/I exceeding 21.0 did meet the fire-resistant criteria of the standard wick test with only one exception of fluid number 72, a phosphate ester. Although this fluid failed the standard wick test, it required much higher concentration (24% by volume) of oxygen to

sustain combustion in O/I test. The result is obviously confusing and before any generalization can be made, more testing will be required in order to reach a definite conclusion. We have noticed in the past that the standard wick test is somewhat sensitive to the duration of tape soaking time before the test is commenced. It would appear that the same is not true in the case of the oxygen index method. Table 2 indicates that wick "soaking time" prior to testing has very negligible influence on the O/I numbers. This inference is drawn from trials on one fluid only and therefore, it must be accepted with caution.

Even though the O/I numbers obtained in this study are indicative of the relative fire-resistance of various types of fluids, it is not expected that such indices would represent absolute numbers. This is due to the fact that a change in the ASTM test procedure may have disturbed the heat energy balance required for the purpose, however, the total volumeteric flow of mixed gases rising in the vertical column was maintained within the specification range. It was also noticed in the equipment specification that only a drastic change in the heat energy balance would adversely influence the test results. Therefore, it is reasonable to assume that a slight change in energy balance due to the use of a special steel holder did not affect the O/I numbers. Besides, we also noticed that the graduated scales on the flowmeters were rather impossible to read for precision better than 1.0 unit. Only an estimate was made where the flow ratings were in fractions of a unit.

In spite of the above difficulties, we have achieved repeatable results in earlier work concerning other materials e.g. conveyor belts and mine ventilation brattice cloth. It is therefore reasonable to apply a tolerance of $\pm$ 0.5 units on all O/I numbers obtained by using the equipment employed in this study.

It is also worth recording that the study done by General Electric Co (1) did not use wicks for O/I tests. Instead, a crucible was used and the ignition was obtained by applying direct flame on the fluid surface without preheating. Due to these reasons and because they did not include hydraulic fluids in their study, it is difficult to make a direct comparison with our investigation. It appears from the G.E.research (1) that oxygen index method could be used for designing

fire-resistant products with a desired O/I number by changing contents of the various fire retarding ingredient in the total product formulation. Therefore, the oxygen index apparatus could serve as a research tool for designing new and less hazardous hydraulic fluids besides serving as a quality assurance tool for verification of the product formulations, once the product has been approved and certified by CEAL.

Conclusions

Using a modified version of the ASTM standard and test procedure in this investigation, it has been demonstrated that it is possible to obtain relative index of flammability of various hydraulic fluids. A reasonable degree of repeatability and a precision within $\pm$ .5 O/I units limited by the graduations on the flowmeters, is achieved.

The O/I numbers obtained in this study may not represent the absolute values of fire-resistance due to a slight change in the test procedure recommended by the manufacturer of the apparatus. The important consideration is that a repeatability of the numbers can be established for the same products and that the relativity of the fire-resistance represented by the O/I numbers still holds good.

Because of the limited study in this investigation, it is not possible to establish any correlation between the O/I test and the standard wick test being used for certification purposes, although there is good agreement in the test results from these two procedures based on qualitative judgement alone (Table 1). It is, however, known from experience with other fire-resistant materials that O/I test provides more consistent results and is therefore more reliable from a scientific point of view.

Recommendations

The procedure used in this investigation for determination of O/I for hydraulic fluids should be adopted in the interim, including all fluids submitted for certification purposes. This practice

will assist in the establishment of a base line of O/I numbers which could be used later for verification of any changes in the product formulations as an aid to the quality assurance program, at CEAL. Any fluid which indicates variation exceeding $\pm$ 2 units compared to the original O/I value should be treated as suspect.

Further research should be undertaken to determine a correlation between the standard wick test and the O/I procedure followed in this investigation. Since the standard wick test presently employed for certification is neither very reproducible nor very reliable, it would be desirable to replace it with the proposed O/I method subject to approval by the relevant CSA committee.

Since difficulty was experienced in holding the oil soaked wicks in a vertical position, particularly when the wick projections were 75 mm or more, it is suggested that a glass rod should be used as a support with the tape wrapped around it. This may facilitate wick projections as long as 125 mm above the tube reservoir and thus allow a look at the flame propagation parameter as well.

Preheating of the fluids, particularly the emulsion types would assist in reducing the flame contact time before ignition takes place. It is recommended that 40 °C should be used as the initial temperature prior to the flame contact.

References

1. Oxygen index of liquids-techniques and applications. By: G.L.Nelson and J.L.Webb, General Electric Co, N.Y. published in Journal of Fire and Flammability, Vol 4(July 1973), p 210.

2. Instruction Manual for Oxygen Index Tester model No: 8100, for flammability of plastics in accordance with the ASTM standard D2863 and produced by United States Testing Co, Inc.

3. "Fire-resistant Hydraulic Fluids" A National Standard of Canada CAN/CSA- M423/M87.

Table 1 - Oxygen Index of Hydraulic Fluids

CEAL Number	Fluid Category	Wick Extension in mm	Soaking Time in hrs	Flame Spread in mm	Std Wick Flame	Oxygen Index ± .5
31	Org Ester	50	2.0	30	Failed	18.5
75	Silicon	65	2.0	75	Pass	21.0
72	Phos Ester	60	2.0	60	Failed	24.5
173	Synthetic	75	1.5	75	Pass	25.0
132	Inv Emulsion	75	5.0	---	Pass	22.5
150	" "	90	6.0	90	Pass	22.7
164	" "	90	2.0	65	Pass	23.5
169	" "	90	2.0	75	Pass	24.5
166	Water Glycol	65	2.0	65	Pass	28.0
171	" "	75	1.0	50	Pass	28.5
172	" "	75	2.0	65	Pass	29.0
133	" "	90	2.0	50	Pass	30.0

Note: All dimensions are approximate.

Table 2 - Oxygen Index ~ Wick Soaking Time

Fluid sample # 164, Invert Emulsion

Soaking Time in hrs	Wick Extension in mm	Flame Propagation in mm	Oxygen Index ± .5
2.5	80	60	23.5
4.5	75	60	23.5
7.0	80	60	23.5
24.0	75	65	24.0

Note: All dimensions are approximate.

Table 3 - Gas Flow Rates In cm /s For Standard Velocity of 4.0 cm/s
(tube diameter is 76.1 mm)

O-Index	N	O_2	O-Index	N	O_2
15	154.6	27.3	32.5	122.8	59.1
15.5	153.7	28.2	33	121.9	60.1
16	152.8	29.1	33.5	121.0	60.9
16.5	151.9	30.0	34	120.1	61.8
17	151	30.9	34.5	119.1	62.8
17.5	150.1	31.8	35	118.2	63.7
18	149.2	32.7	36	116.4	65.5
18.5	148.2	33.7	37	114.6	67.3
19	147.3	34.6	38	112.8	69.1
19.5	146.4	35.5	39	111.0	70.9
20	145.5	36.4	40	109.1	72.8
20.5	144.6	37.3	41	107.3	74.6
21	143.7	38.2	42	105.5	76.4
21.5	142.8	39.1	43	103.7	78.2
22	141.9	40.0	44	101.9	80.0
22.5	141.0	40.9	45	100.0	81.9
23	140.1	41.8	46	98.2	83.7
23.5	139.1	42.7	47	96.4	85.5
24	138.2	43.7	48	94.6	87.3
24.5	137.3	44.6	49	92.8	89.1
25	136.4	45.5	50	91.0	91.0
25.5	135.5	46.4	51	89.1	92.8
26	134.6	47.3	52	87.3	94.6
26.5	133.7	48.2	53	85.5	96.4
27	132.8	49.1	54	83.7	98.2
27.5	131.9	50.0			
28	131.0	50.9			
28.5	130.1	51.8			
29	129.1	52.8			
29.5	128.2	53.7			
30	127.3	54.6			
30.5	126.4	55.5			
31	125.5	56.4			
31.5	124.6	57.3			
32	123.7	58.2			

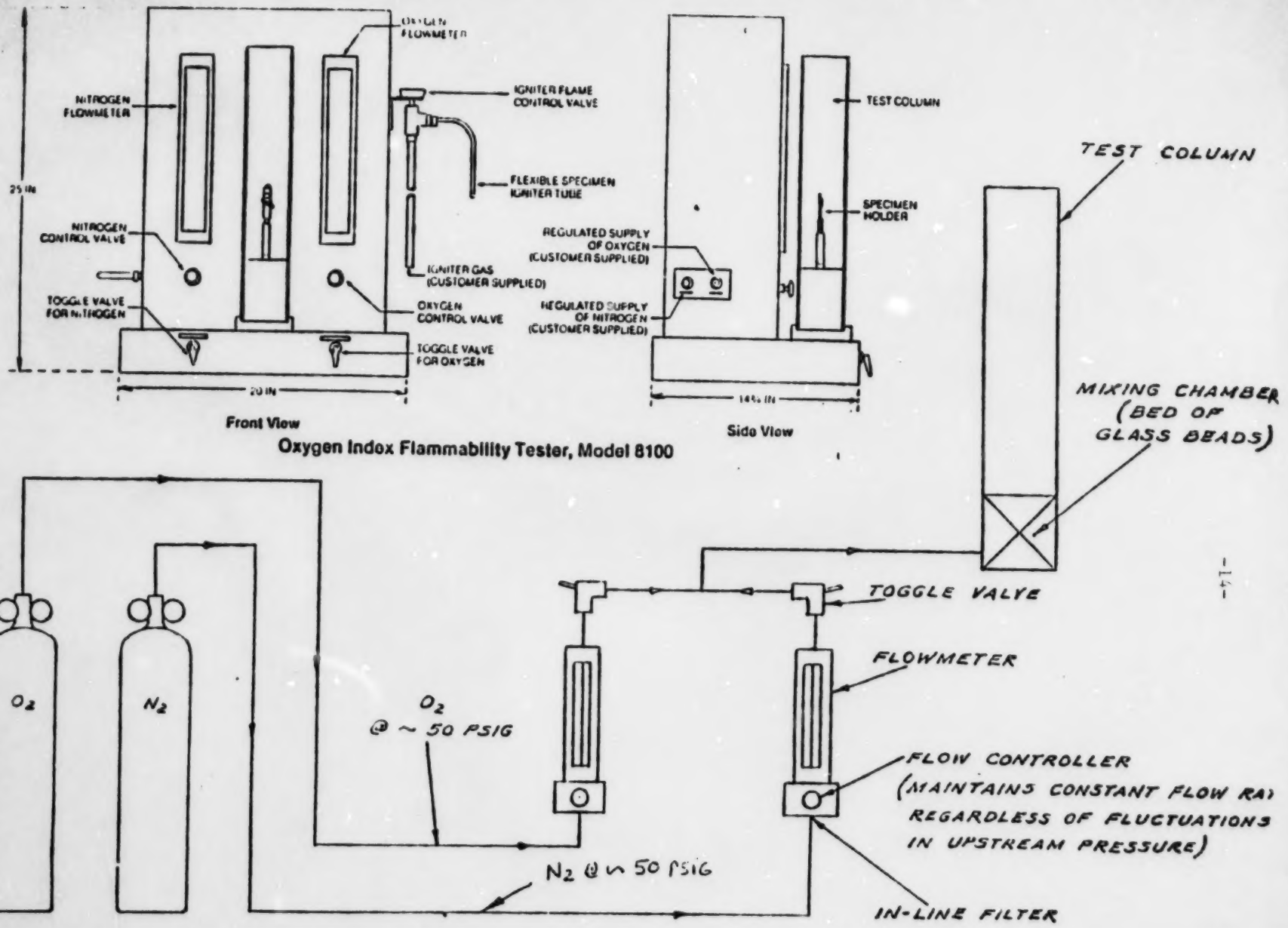

Figure 1: Oxygen Index Flammability Tester, Model 8100

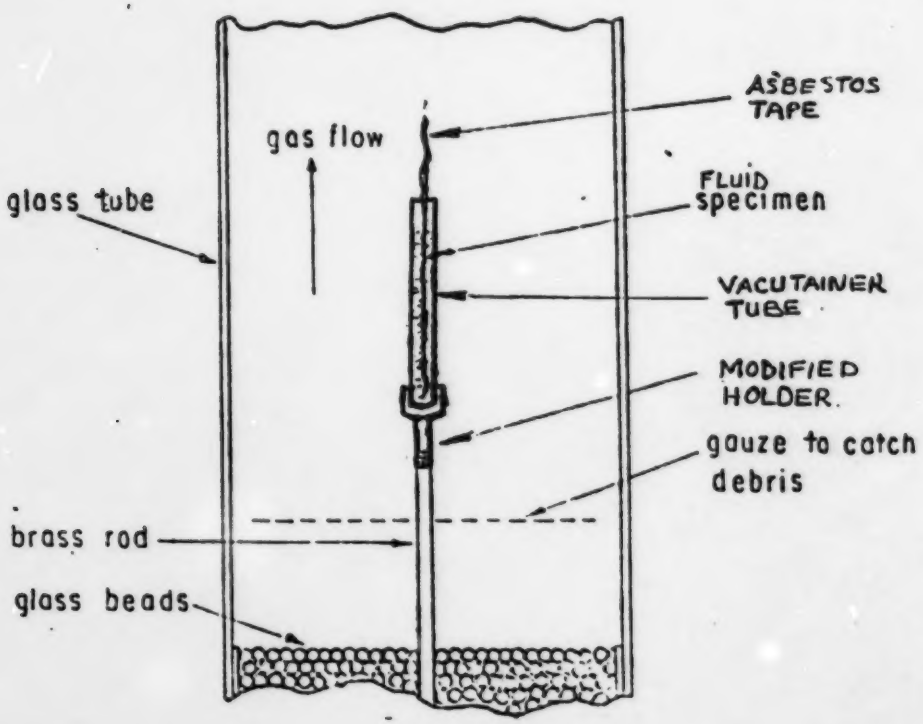

Figure 2: Arrangement of Specimen in the chimney.